

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE		3. REPORT TYPE AND DATES COVERED <i>Final 15 Aug 89 - 15 May 93</i>
4. TITLE AND SUBTITLE Integrated Synthesis and Post-Processing of SiC and AlN			5. FUNDING NUMBERS <i>DAAL03-89-K-0131</i>	
6. AUTHOR(S) A.I. Kingon, R. F. Davis and A. K. Singh				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) North Carolina State University Department of Materials Science and Engineering Raleigh, NC 27695-7919			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING/MONITORING AGENCY REPORT NUMBER <i>ARO 26673.9-MS-A</i>	
11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Synthesis of nanocrystalline powders of SiC, AlN, Si Si ₃ N ₄ , TiN, TiC, TiO ₂ have been achieved by a non thermal microwave plasma reactor from vapor phase precursors. In the case of TiO ₂ the phase can be a metastable high pressure plasma (β -TiO ₂). Nanoparticles of Si and SiO _x displayed strong red-orange photoluminescence. Two mechanisms for photoluminescence were identified one based on 3-D quantum confinement and a second based on natural surface oxides. Creep of fine-grained (0.7 μ m) AlN has been studied for the first time. The mechanism was identified as being diffusion-accommodated grain-boundary sliding.				
14. SUBJECT TERMS Synthesis; plasma processing; nonoxides; SiC; AlN; TiN; TiC; nanoparticles; Si photoluminescence; creep of AlN			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

INTEGRATED SYNTHESIS AND POST-PROCESSING OF SiC AND AlN

FINAL REPORT

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U. S. ARMY RESEARCH OFFICE

DAAL 03-89-K-0131

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STATEMENT OF THE PROBLEMS STUDIED

The general theme of the research is the synthesis and characterization of the properties of nanocrystalline materials. The specific objectives of this three-year project has been twofold. The first problem that was addressed was the synthesis of nanosize refractory ceramic powders of aluminum nitride, silicon carbide, titanium carbide, and titanium oxide. This was demonstrated for the first time using a nonthermal microwave plasma for the decomposition of vapor phase precursor gases under laminar flow conditions. Then, as a result of intense interest in photoluminescence in "porous Si", we shifted emphasis to a second, related problem, viz that of the characterization and origin of unique orange-red luminescence observed in nanosize particles of Si and SiO_x also synthesized by the microwave plasma technique.

SUMMARY OF RESULTS

Initially after constructing the system as shown in one of its configurations in Figure 1, the microwave plasma was characterized using a Langmuir probe analysis. This study indicated that optimum plasma stability was achieved at a net 100 Watts of plasma power and a 1 Torr argon system pressure. Under these conditions, measured values of electron density were $5 \times 10^{11} / \text{cm}^3$ and electron temperatures of about 1.5×10^4 K.

In the first stage of this investigation, it was demonstrated that high purity nanosize refractory ceramic powders could be synthesized using a nonthermal microwave plasma and vapor phase precursors. The first powders to be synthesized were those nonoxide refractories of aluminum nitride, silicon carbide and silicon nitride. Single crystal particles of about 5 nm in diameter were grown and characterized using transmission electron microscopy (TEM), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS). The particle size distributions were shown to be small. The flow conditions of the reactor minimize particle-particle impact and the subsequent neck growth between particles, which is a deleterious factor in **thermal** plasma synthesis schemes. Later, nanoparticles of titanium nitride and titanium oxide were synthesized and characterized using TEM and AES.

Characterization of the particles indicated that aluminum nitride could be formed in either hexagonal or cubic phases depending on nitrogen gas concentration. SiC was the low temperature beta cubic phase and Si_3N_4 was primarily the alpha phase. In both cases the reaction proceeded via initial nucleation of Si clusters and further reaction to form the carbide or nitride. Titanium nitride could be synthesized as either cubic (TiN) or tetragonal (Ti_2N), depending once

again on nitrogen gas concentration. Titanium oxide powder was primarily formed in the rutile (tetragonal) phase, although small quantities of other phases were identified.

Powder collection methods were also investigated. It was found that the silicon nanoparticles could be attracted to a positively biased, electrically conductive substrate placed on a substrate heater or on electrostatic precipitator plates located within the quartz reaction chamber tube. Under most conditions, a bias voltage of +200 VDC was sufficient to capture the majority of the particles traveling in the gas stream. In addition, it was found that particles could be collected on nonconducting substrates when these substrates were placed partially immersed the plasma region in the reactor.

The cubic form of Si and amorphous SiO_x were later grown to investigate photoluminescence behavior. Characterization included high resolution TEM and X-ray diffraction (XRD) and particle histograms showing particle size distribution statistics were developed. Further investigations revealed a correlation of particle size with system pressure and flow rates.

Altogether, in the first stage of the investigation it was demonstrated that a variety of ceramic powders could be synthesized in nanosize form using this new versatile process. In addition, control of particle size and crystalline morphology was displayed.

Because a major application for the nonoxide powders is high temperature ceramics, we initiated a first study of the high temperature creep of AlN. The operative and controlling mechanisms of steady-state creep in hot-pressed AlN were determined both from kinetic data within the temperature and constant compressive stress ranges of 1470 to 1670 K and 100 to 370 MPa, respectively, and from the microstructural results of TEM. No secondary phases were detected in the bulk or at grain boundaries using Raman spectroscopy and high resolution electron microscopy. The stress exponent was approximately 1.0 at all temperatures. The activation energies ranged between 558 and 611 kJ/mol. The most prominent microstructural features of the crept samples were elongated grains, strain whorls, and triple point folds. Dislocations were generated only at the strain whorls in order to relieve the localized stress by intraboundary mechanical interaction among the grains. They contributed little to the observed deformation. The controlling mechanism for creep was diffusion-accommodated grain-boundary sliding. This mechanism was accompanied in parallel by relatively small amounts of unaccommodated grain-boundary sliding. Cavitation was not observed.

In the second stage of this investigation, the photoluminescence of Si and SiO_x nanoparticles were explored. It was shown that strong orange-red luminescence could be observed in Si and SiO_x nanoparticles at 300 and 77 K temperatures. Time-integrated and time-resolved photoluminescence together showed a luminescence peak at 840 nm and a radiative decay lifetime of approximately 1 ns. In addition, such luminescence was stable with time in air and with annealing up to 1000°C in an inert atmosphere.

Further investigations into the luminescence from these nanoparticles were conducted in order to understand the mechanism for luminescence in these particles. To help distinguish between a mechanism based on chemical surface effects or quantum size confinement effects, particles of SiO_x, displaying no detectable crystallinity, were grown and particles of a large mean diameter synthesized. Such particles were not expected to luminesce at the same wavelength as smaller crystalline particles if quantum size played a roll in the luminescence. This, in fact, was shown not to be the case since both the amorphous and the larger diameter particles displayed the same luminescence peak. The conclusion was drawn that the *primary* mechanism for the visible photoluminescence in Si nanoparticles was a direct result of the formation of a naturally occurring amorphous oxide coating forming shortly after their exposure to the terrestrial atmosphere. Most recently we have identified a second less efficient mechanism under low laser pumping power densities that seems to be size dependent for particle sizes less that about 5 nm.

Under an accompanying AASET program we are now investigating the application of various nanoparticles in several device structures, such as electroluminescent and cathodoluminescent devices.

SUMMARY OF MAJOR ACCOMPLISHMENTS

1. First demonstration of the synthesis of crystalline, nanosized particles by gas phase reaction in a microwave plasma reactor.
2. First microwave plasma gas phase synthesis of single crystal nanoparticles of Si, Si₃N₄, SiC, TiC, TiN, AlN, and TiO₂.
3. Development of electrostatic methods for the recovery of nanoparticles from the gas stream.
4. First characterization of the high temperature creep of AlN.
5. First demonstration of photoluminescence in nanoparticles of Si.
6. Demonstration that there are two photoluminescence mechanisms which can be observed in nanoparticles of Si, and demonstration that the mechanism which results in the greatest

photoluminescence intensity is related to the presence of surface oxide. The results are also relevant to porous Si.

LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

Angus Kingon	principal investigator
Robert F. Davis	principal investigator
A.K. Singh	visiting professor
Ken Hsieh	postdoctoral researcher
Dan Lichtenwalner	postdoctoral researcher
Prabjot Mehta	student, received M.S. in materials science and engineering, 1993
Peter Milewski	current student, PhD. expected 1995 (now supported by linked AASET funding)
Dahua Zhang	student, received PhD. in electrical engineering, 1993 (portion of her PhD. research was conducted within this project)
A. Vasudev	student, received M.S. in materials science and engineering, 1991
K.S. Ailey-Trent	student, PhD. expected 1994 (a portion of her thesis research was conducted within this project)

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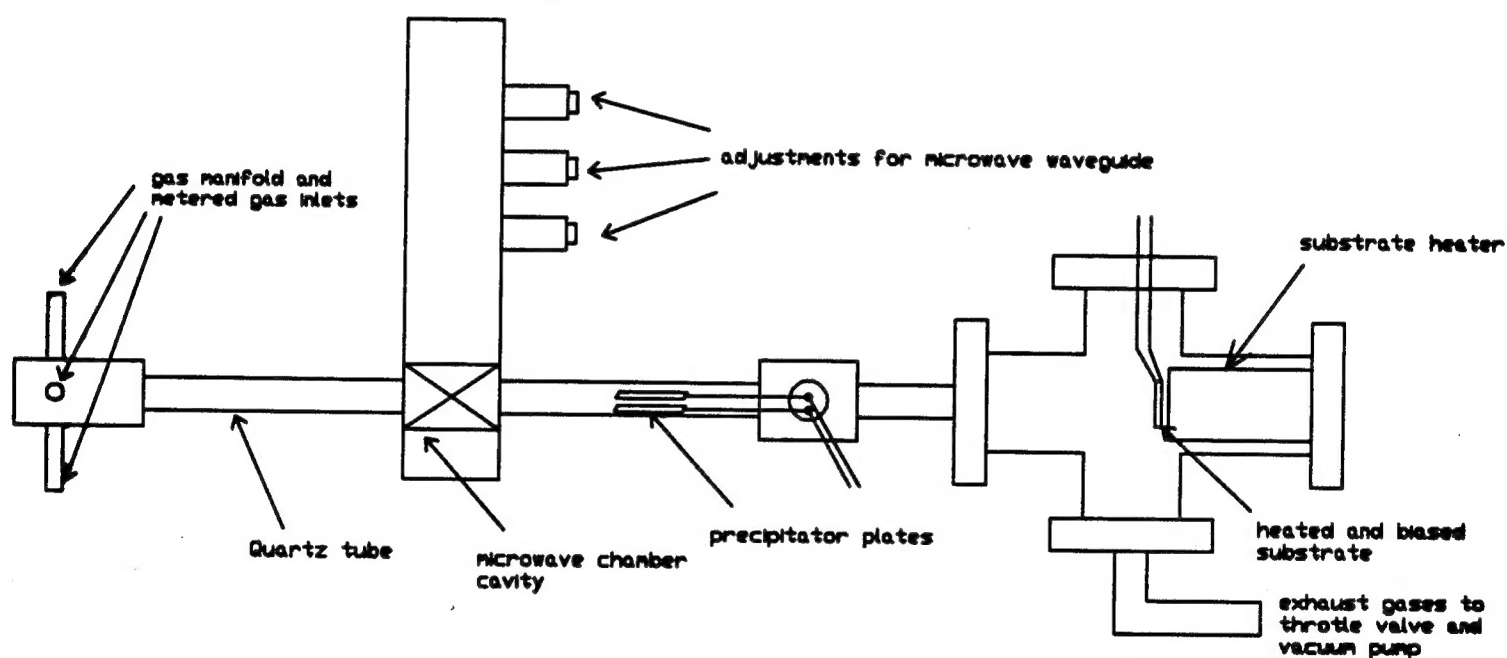


Figure 1. Nonthermal Microwave Particle Synthesis System Schematic

APPENDIX

(Enclosed are a copy of the first page for each of the published articles)

SYNTHESIS OF SiC CLUSTERS IN A NONTHERMAL MICROWAVE PLASMA

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ABSTRACT

A new technique has been developed to condense nanoparticles (clusters) of SiC and other nonoxide materials in a nonthermal microwave plasma. The experimental rationale and approach is described. It utilises silane and acetylene precursors in an Ar diluent, with the synthesis carried out in a microwave plasma at a pressure of ~1 torr. The plasma conditions have been characterised, as have the effect of important parameters (gas ratios, flow rates and pressure) on the product nanoparticles. The resultant nanoparticles have been characterised ex-situ by TEM, Auger, and XPS spectroscopy. SiC particles collected are ~5nm in size, with cubic, hexagonal and rhombohedral polytypes observed. Silicon nitride has been synthesised similarly by using silane and nitrogen as the precursor gases. Implications of the new technique are discussed.

INTRODUCTION

SiC and Si₃N₄ are ceramic materials which are gaining commercial acceptance in place of critical metal components in an increasing range of applications. These applications utilise their unique material properties, in particular low density, high temperature strength and creep resistance, and excellent wear and corrosion resistance [1-4].

The ceramics are prepared by sintering of powders. This requires viable techniques for powder synthesis. In case of SiC powder, synthesis is by direct carbothermal reduction of SiO₂. The resulting powder is coarse-grained and contains defects [5] and impurities. Alternative gas phase synthesis methods have been investigated, including synthesis in thermal plasma torches [6] and laser synthesis [7-10]. This former method has been generally unsuccessful, because of large temperature, velocity, and compositional gradients within the thermal plasma. The resulting powders have been highly agglomerated, chemically inhomogeneous, and difficult to sinter.

The objectives of the present research project are two-fold: 1). To determine whether crystalline nonoxide powders such as SiC and Si₃N₄ can be synthesised in a nonthermal plasma under conditions which maintain laminar flow, and to characterise the resulting powders; 2). To determine unique properties which may be displayed by these particles when they are nano-sized (less than 10nm). This paper presents only the results of research into the first objective.

EXPERIMENTAL

Reactor System and Gas Flow

The experimental apparatus (Fig.1) consisted of a long (7 ft.) quartz tube (O.D. = 38 mm, I.D. 35 mm) which was inserted into a circular applicator of a microwave source (S-1500 Astex) capable of 1.5 KW. This tube was connected to the mass flow controllers on one end and the vacuum pump fitted with automatic throttle valve pressure controller on the other. The system could be purged with Ar and/or N₂ and similarly the exhaust gases diluted.

The SiC was synthesised by triggering the microwave plasma (50-100 watts) in a laminar flow of the mixture of C₂H₂, SiH₄ and Ar. The optimum flow rates were determined to be 10 standard cubic centimeters per minute (sccm) of SiH₄, 4 sccm of C₂H₂, and 160 sccm of Ar in the case of SiC and 5 sccm of SiH₄, 15 sccm of N₂, and 50 sccm of Ar in case of Si₃N₄. Laminar flow is maintained at these flow rates. It should be noted that these rates do not quite correspond to thermodynamic stoichiometric ratios. We deduce that this is due to more difficult excitation of SiH₄ compared to that of C₂H₂.

The optimum flow ratios were determined by compositional analysis performed by Auger electron spectroscopy of the collected particles. Higher C₂H₂ flow rates resulted in excess carbon.

SYNTHESIS OF NONOXIDE CERAMIC POWDERS BY NONTHERMAL MICROWAVE PLASMA

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ABSTRACT

We report the synthesis of nonoxide ceramic powders of aluminum nitride, silicon carbide and silicon nitride by nonthermal microwave plasma of precursor gases under conditions of laminar flow. The precursor gases used were trimethyl aluminum and nitrogen for aluminum nitride, silane and acetylene for silicon carbide, and silane and nitrogen for silicon nitride. The argon gas was used as the diluent/carrier gas in all the cases. The effect of flow rate of the gases and hence the effect of concentration and residence time of the activated species in the plasma is discussed. The microwave energy in the plasma was (50-100) Watts. The product particles were characterized by transmission electron microscopy, Auger electron spectroscopy and X-ray photoelectron spectroscopy.

The synthesized material was found to be ultrafine (~5nm) and crystalline. Aluminum nitride stabilized in either hexagonal or cubic phases depending on the nitrogen concentration.

The silicon carbide formed was mostly cubic-3C accompanied with several hexagonal and rhombohedral polytypic modifications. The implications of the occurrence of polytypes in particles of nanometer size are discussed in terms of the existing theories.

The silicon nitride was formed in the α phase modification.

I. INTRODUCTION

Aluminum nitride, silicon carbide and silicon nitride are well known ceramics which can stand high temperature and offer high strength and resistance to corrosion. They are being used to replace metals with an advantage of being of lower density (1-6). Also they are being applied to the microelectronic devices in thin film form (7,8).

The high temperature processing of these ceramics introduces a variety of defects, consequently the properties of the ceramics are greatly limited. Particularly, in silicon carbide the abundance of polytypes and phase transformations amongst them develop an additional complication. These phase transformations often result in undesirable changes in microstructure including exaggerated grain growth (9). The defects compromise the mechanical strength and thermal properties of the materials. Many of the defects originate from the milling (Acheson process for silicon carbide), presence of hard agglomerates and post firing machining. As a result, several groups have embarked upon gas phase synthesis (10) using thermal plasma torches and laser (11-14) to produce nanoscale particles. However, the former method has generally been

NONTHERMAL MICROWAVE PLASMA SYNTHESIS OF CRYSTALLINE TITANIUM OXIDE & TITANIUM NITRIDE NANOPARTICLES

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ABSTRACT

We report the nonthermal synthesis of ultrafine crystalline nanoparticles of titanium oxide and titanium nitride. The nanoparticles are formed by gas phase reactions between precursor gases dissociated in the microwave plasma. For the production of titanium nitride, titanium tetraisopropoxide (TTIP) and ammonia or nitrogen precursor gases are used. For titanium oxide production TTIP and oxygen are used as precursor gases. In both cases ultrahigh purity argon serves as a carrier gas and diluent. Transmission electron microscopy (TEM) revealed that the titanium nitride powders so formed were either cubic (TiN) or tetragonal (Ti₂N) depending on the operational conditions, particularly the relative nitrogen gas flow rates. Ammonia gas was found to be a much more reactive nitrogen source than molecular nitrogen gas. For the titanium oxide growth an excess of oxygen was utilized to achieve TiO₂. Powders collected from the gas phase corresponded to the rutile (tetragonal) phase. However, powders collected from the cavity walls corresponded to the high temperature and pressure (orthorhombic) β -TiO₂. There was also evidence of a polytypically modulated phase of TiO₂, with the observed c-periodicity double the parent c-periodicity of the rutile phase. Using a low oxygen flow rate during powder formation led to the formation of orthorhombic Ti₃O₅ "powders". The powders were easily sinterable by *in situ* electron beam annealing in the electron microscope, with an estimated temperature of around 550°C. This is much lower than the temperatures normally required to sinter these materials.

1. INTRODUCTION

Titanium nitride (TiN) is an important material for advanced refractory applications. TiN powders are often used as reinforcements in metal, ceramic and polymer matrix composites [1]. Gas phase production of titanium nitride powder has been reported previously [2,3]. In these previous reports, high temperature processing is necessary, and the resulting powder sizes are in the micron range.

Titanium oxide is being used in many applications due to its high dielectric constant, high refractive index and high chemical stability. It is used as filters in visible and near infrared wavelength, insulating coatings, photoanodes, memory cells, capacitors of high dielectric constant, antireflecting coatings and wave guides, etc. In fine particle state these can be used as pigments, magnetic compounds for recording sound and images, thickening and reinforcing agents, fuel pellet powders for nuclear plants, in catalysis, in automobile parts and in piezoelectric materials [1-7]. There are several papers describing the synthesis of titanium oxide chemically, thermally, or by laser [4,5].

This paper describes the synthesis of ultrafine crystalline powders of titanium oxide and titanium nitride using a nonthermal microwave plasma. Precursors titanium tetraisopropoxide (TTIP) and molecular oxygen were used to synthesize titanium oxide powders, while TTIP and ammonia or molecular nitrogen were used for titanium

VISIBLE LIGHT EMISSION FROM SILICON NANOPARTICLES

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ABSTRACT

Orange-red light emission has been observed for the first time from crystalline silicon nanoparticles produced by gas phase synthesis in a non-thermal microwave plasma. The size and crystalline nature of the particles have been confirmed by transmission electron microscopy and X-ray diffraction. Photoluminescence at 300 K and 77 K has been measured and analyzed. The emission spectra are consistent with quantum mechanical calculations based on a quantum box.

INTRODUCTION

Recently there has been considerable interest in visible light emission from silicon (Si) nanostructures.^{1,2,3} Most recent reports have concentrated on porous Si quantum wire structures, although the earliest reports focused on microcrystalline Si:H.³ In this paper, the luminescence and structural properties of crystalline silicon nanoparticles produced by gas phase synthesis are presented. Visible orange-red light emission has been observed. The Si nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and both time-integrated and time-resolved photoluminescence. A simple quantum mechanical calculation based on a quantum box is presented.

EXPERIMENTAL PROCEDURE

The crystalline silicon nanoparticles examined were prepared using a non-thermal microwave plasma reactor⁴. Electronic grade silane (SiH₄) was used as the precursor gas, and ultrahigh purity argon (Ar) served as a carrier gas and a diluent. A mixture of 10 sccm SiH₄ and 90 sccm Ar were used, with the system pressure held at 1 torr and a plasma power of 150 watts. The gas flow was laminar, allowing the particles produced in the plasma region to be carried downstream where

Visible Light Emission from Silicon and Silicon Oxide (SiO_x) Nanoparticles

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Nanosize particles of silicon and silicon with oxygen were synthesized from the gas phase precursors silane and oxygen using a 100 Watt nonthermal argon microwave plasma. Oxygen dopant reactant gas flow rates were varied from zero to twice the molar flow rate of silane. Mean particle sizes were varied from approximately 7–20 nm by changing the reactor pressures from 1–8 Torr respectively. Particles were collected from the reaction chamber walls in the vicinity of the microwave plasma, or downstream from the plasma on electrostatic precipitator plates. The particles were characterized to determine their mean diameter, size distribution, crystallinity and crystalline phase using Transmission Electron Microscopy (TEM), Selected Area Diffraction (SAD), and X-Ray Diffraction (XRD). Orange-red light emission has been previously observed in silicon nanosize particles¹⁻⁴. The present study has shown that particles grown with up to twice the molar flow rate of oxygen to silicon, characterized as highly amorphous, exhibit no noticeable decrease in the optical PL. This also been shown to be the case for particles grown to diameters up to 20nm. These results have implications for the mechanism of PL in silicon nanoparticles.

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Kinetics and mechanisms of high-temperature creep in polycrystalline aluminum nitride

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(Received 2 March 1992; accepted 30 December 1992)

The operative and controlling mechanisms of steady-state creep in hot-pressed AlN have been determined both from kinetic data within the temperature and constant compressive stress ranges of 1470 to 1670 K and 100 to 370 MPa, respectively, and from the microstructural results of TEM. No secondary phases were detected in the bulk or at the grain boundaries using Raman spectroscopy and HREM. The stress exponent was ≈ 1.0 at all temperatures. The activation energies ranged between 558 and 611 kJ/mol. The most prominent microstructural features of the crept samples were elongated grains, strain whorls, and triple-point folds. Dislocations were generated only at the strain whorls in order to relieve the localized stress caused by intraboundary mechanical interaction among the grains. They contributed little to the observed deformation. The controlling mechanism for creep was diffusion-accommodated grain-boundary sliding. This mechanism was accompanied in parallel by relatively small amounts of unaccommodated grain-boundary sliding. Cavitation was not observed.

I. INTRODUCTION

AlN crystallizes in the close-packed wurtzite structure ($a = 0.311$ nm, $c = 0.498$ nm). It possesses a slightly distorted, polar, noncentrosymmetric crystal structure consisting of two interpenetrating lattices of Al and N atoms which form metal and nonmetal sublattices that are displaced from each other by $0.385[0001]$.^{1,2} Of the 12 possible tetrahedrally coordinated sites in the N sublattice, Al can fill either the six upward- or the six downward-pointing sites. Only one type of tetrahedral site will be filled by the Al atoms in any given grain to minimize electrostatic repulsion.

Hot-pressed AlN possesses excellent thermal conductivity (≈ 200 Wm⁻¹K⁻¹),³ a low dielectric constant ($\epsilon' = 9.2 \pm 0.05$),⁴ and a coefficient of thermal expansion ($43 \times 10^{-7}/\text{K}$)⁵ close to that of Si within the temperature range 293–473 K.⁶ These properties, combined with good mechanical strength (250–500 MPa to 1773 K),^{7,8} make AlN a favored candidate as a substrate material for electronic packaging. The creep behavior of AlN at elevated temperatures is also of interest in terms of potential structural applications both alone and combined in-solid solution with other ceramics such as SiC.^{9,10}

All investigations concerned with the creep of AlN (including that reported herein) have used hot-pressed polycrystalline material. Spivak *et al.*^{11,12} were the first to report the creep behavior of this material (average grain size ≈ 1 μm). The text of their paper implied that no additional phases were added to at least one of their materials. Four-point bending was employed using a fixed stress of 9.8 MPa over a temperature range of 1873 to 2073 K. An activation energy of ≈ 460 kJ/mol was reported. The mechanism of creep was attributed to a combination of diffusion and viscous flow. Nishida and Nishikawa¹³ used a three-point bending approach on material containing no sintering additives. Their study resulted in activation energies from 400 to 460 kJ/mol and stress exponents from 1.0 to 1.2 for dense samples and 1.3 to 1.6 for porous samples. It was concluded that diffusion was the controlling creep mechanism. A more recent deformation study using samples having a particular average grain size between 1.8 and 19 μm and produced by hot pressing between 2173 and 2400 K was conducted in four-point bending by Jou and Virkar.¹⁴ No sintering aids were intentionally introduced into this material during processing. It was concluded that creep in this material in the temperature

Light Emission from Crystalline Silicon and Amorphous Silicon Oxide (SiO_x) Nanoparticles

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Bright orange-red light emission was observed from single crystal silicon nanoparticles and silicon oxide (SiO_x) nanoparticles. The emission peak was recorded at about 1.5 eV both at room temperature and 77K. Varying the mean silicon particle size, we observed no effect of particle diameter on the emission wavelength. Amorphous silicon oxide (SiO_x) nanoparticles also showed essentially the same emission spectrum as the crystalline particles. The absence of change in the photoluminescence (PL) spectrum with variations in particle size and crystallinity indicates that quantum confinement is not the controlling PL mechanism. An examination of the hydrogen content with relation to the PL intensity showed no direct correlation; however, all samples did contain some hydrogen, so its effect on PL cannot be ruled out. To test for the presence of photoluminescent siloxene on the surface of the particles, nitric acid was applied; a violent reaction occurred with the silicon particles, while the SiO_x particles showed no reaction. Taken in conjunction with the emission data, these experiments demonstrate that the PL of the SiO_x is also not dependant on siloxene. Evidence points to an amorphous coating as the source of photoluminescence.

Key words: Light emission, silicon nanoparticles, SiO_x nanoparticles

INTRODUCTION

Bulk silicon has an indirect band gap of 1.1 eV and does not emit radiation in the visible range or at high intensities at any wavelength. However, it has been shown that visible or near-visible light emission can originate from special forms of silicon such as amorphous silicon (a-Si), porous silicon (PS), or silicon nanoparticles. Amorphous silicon is produced by the incorporation of high concentrations of hydrogen during the growth process and has been shown to photoluminesce with a major peak at 1.3 eV and a full width half maximum (FWHM) of approximately 0.3 eV at 77K.¹ Porous silicon, produced by anodic etching of silicon single crystal wafers in an aqueous HF solution, exhibits photoluminescence with a peak at 1.7 eV.^{2,3} In addition, visible photoluminescence (PL)

has been observed in nanosize silicon particles by several researchers.⁵⁻¹⁰ Takagi et al.⁶ produced nanosize single crystal silicon powders by microwave plasma decomposition of silane. Fourier transform infrared analysis (FTIR) revealed that oxidation occurred when the samples were exposed to a humid atmosphere, and that the room temperature PL intensity *increased* and *blue shifted* with longer exposure time. Heath and Jasinski⁷ produced ultrafine crystalline and amorphous powder by laser excited decomposition of disilane. Fourier transform infrared analysis of these powders likewise showed that oxidation occurs when there is exposure to oxygen and that oxidation resulted in a *decrease* in luminescence intensity and a blue shift in peak position. Previously, we reported PL in nanocrystalline silicon powder produced by microwave decomposition of silane with bright visible red-orange luminescence.⁹ In this paper, we present the effects of oxidation or oxygen

(Received August 13, 1993)